

United States Patent

Selman et al.

[15] 3,640,705

[45] Feb. 8, 1972

[54] TREATMENT OF PLATINUM GROUP METALS AND ALLOYS

[72] Inventors: Gordon Leslie Selman; Peter James Ellison, both of London, England

[73] Assignee: Johnson, Matthey & Co. Limited, London, England

[22] Filed: Jan. 30, 1969

[21] Appl. No.: 795,513

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 520,361, Jan. 13, 1966, abandoned.

Foreign Application Priority Data

[30] Jan. 15, 1965 Great Britain 1,882/65

[52] U.S. Cl. 75/172, 148/20.3, 75/122.5

[51] Int. Cl. C22c 5/00

[58] Field of Search 75/172, 135; 148/20.3, 4

[56] References Cited

UNITED STATES PATENTS

2,406,172	8/1946	Smithells.....	75/172 X
2,636,819	4/1953	Streicher	75/172
3,117,894	1/1964	Coxe.....	148/11.5

Primary Examiner—L. Dewayne Rutledge

Assistant Examiner—E. L. Weise

Attorney—Cushman, Darby & Cushman

[57] ABSTRACT

An alloy and method for making the same including alloying with platinum, rhodium, iridium and their mixtures, alone or alloyed with palladium a stable base metal capable of forming a refractory compound. The resulting alloy is heated in the presence of a molecular oxygen containing gas such as air or oxygen at a temperature ranging from 900° to at least 1,200° C. whereby the stable refractory compound is formed internally of said alloy and is dispersed uniformly therethrough.

10 Claims, 3 Drawing Figures

PATENTED FEB 8 1972

3,640,705

SHEET 1 OF 2

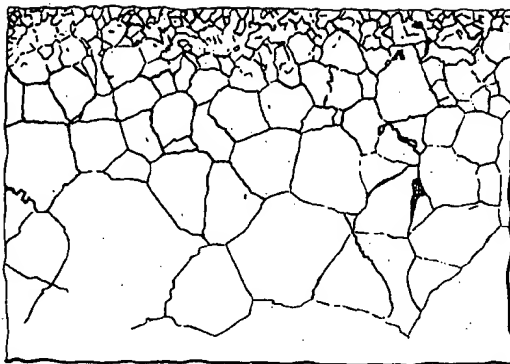


Fig. 1

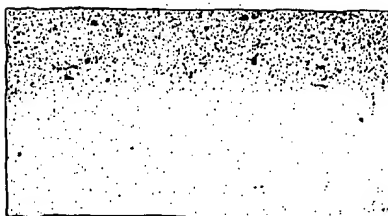
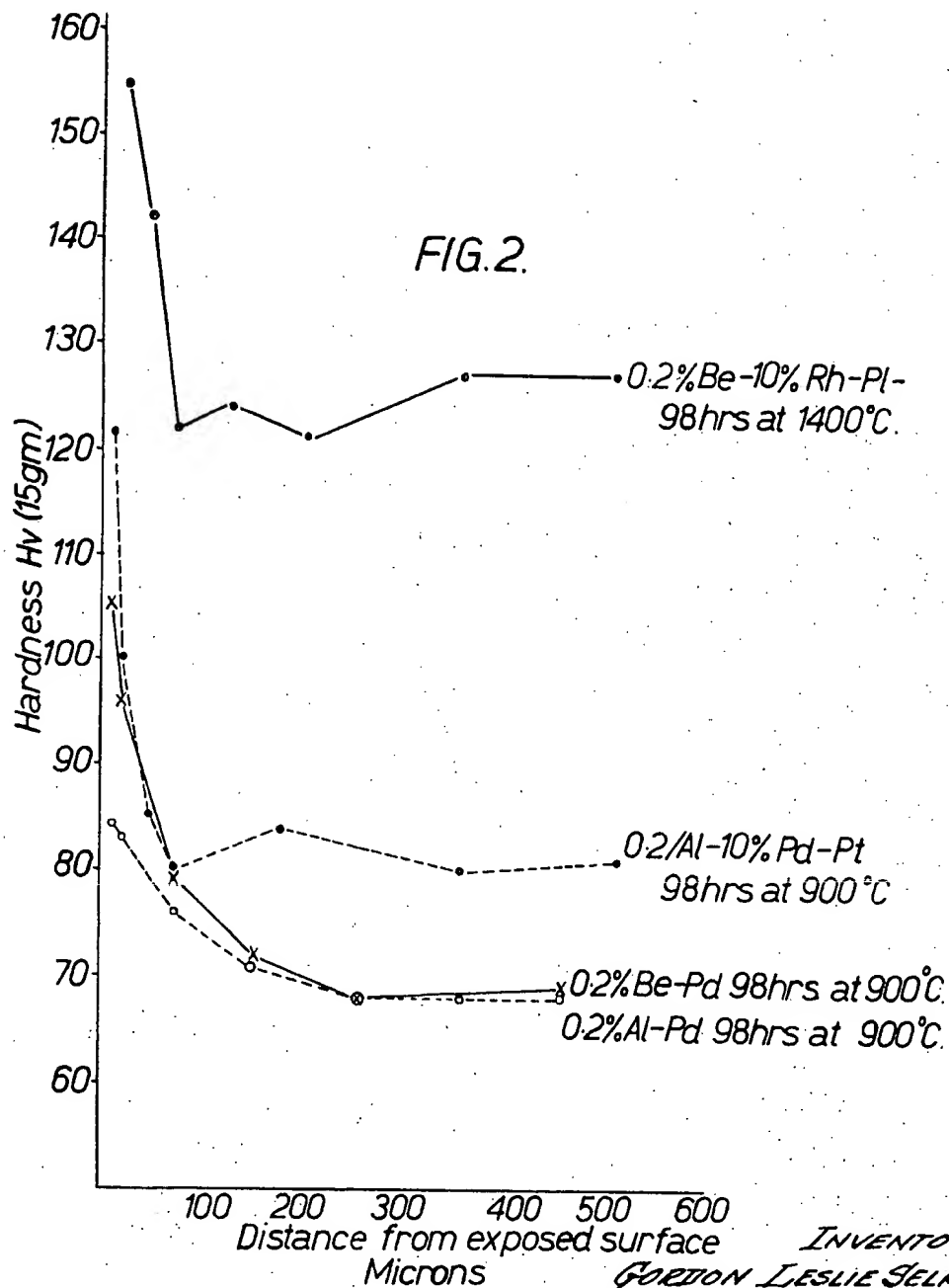


Fig. 3

INVENTORS

Gordon Leslie Selman
Peter James Ellison



INVENTORS
GORDON LESLIE SELMAN
PETER JAMES ELLISON
BY *Cushman, Darby & Cushman*
ATTORNEYS

TREATMENT OF PLATINUM GROUP METALS AND ALLOYS

This application is a continuation-in-part of our application, Ser. No. 520,361, filed Jan. 13, 1966, now abandoned. This invention relates to the treatment of platinum group metals and alloys.

The platinum group metals and alloys of the platinum group metals with one another are much favored for use under conditions involving high temperatures owing to their high melting points and their extremely good resistance to oxidation, such metals and alloys are extensively used in apparatus for the glass industry where they are subjected to the action of air and molten glass, for example, as linings for glass-melting furnaces, and bushings used in the manufacture of glass fibers. Unfortunately, however, these advantageous properties are to some extent offset by the low mechanical strength of these metals under such conditions.

Attempts have, in the past, been made to overcome this disadvantage. For example, it has been proposed to effect a grain stabilization of platinum metal by the addition of nonmetallic substances such as oxides and carbides, to the platinum. Such a procedure involves the separate production of the platinum and the oxide or carbide addition in powder form and their subsequent processing by powder metallurgical methods.

Another method of obtaining increased metallic strength, which has hitherto been applied to base metal and silver alloys, is that known as internal oxidation. The basic requirements for the effectiveness of such a method of strengthening are, firstly, that the main or solvent metal constituent shall dissolve considerable quantities of oxygen without forming a discrete oxide phase and, secondly, that the minor or solute metal, under the same temperature and pressure conditions, will react to form a discrete oxide phase of high stability. Alloys of silver with aluminum, beryllium, thorium and the like satisfy the above conditions and can be effectively subjected to internal oxidation.

The applicants have now surprisingly discovered that platinum, palladium and rhodium alloys containing a minor amount of a solute base metal or metals or platinum group metals alloys containing platinum, palladium or rhodium and a solute base metal, can be internally oxidized to produce a dispersion-hardened material.

The object of this invention, therefore, is to provide an improved platinum group metal alloy, which shall offer increased mechanical strength at elevated temperatures.

Another object of the invention is to provide a method of improving the high-temperature properties of platinum group metal alloys.

A further object is to provide an improved palladium or rhodium alloy or composition or a platinum group metal alloy or composition containing platinum, palladium or rhodium exhibiting the properties of oxidation resistance and high mechanical strength at elevated temperatures.

A still further object is to enable platinum group metal alloys or compositions having improved properties to be produced by powder metallurgical procedures.

According to one feature of this invention, therefore, an alloy or composition having the properties of oxidation resistance and high mechanical strength at elevated temperatures comprises alloying a metal selected from the group consisting of platinum, rhodium, iridium and their mixtures, alone

and alloyed with palladium, with at least one member capable of forming a stable refractory compound and selected from the group consisting of beryllium, magnesium, aluminum, silicon, thorium, uranium, metals in the first transition series consisting of calcium through nickel, metals in the second transition series consisting of strontium through molybdenum and metals in the third transition series consisting of barium through tantalum, said member being present in an amount ranging from a trace to 5 percent by weight of said alloy, heating said alloy in the presence of a gas containing molecular oxygen at a temperature ranging from about 900° to at least 1,200° C. whereby said stable refractory compound is formed internally of said alloy and is dispersed uniformly therethrough.

Any base metal capable of forming a ductile alloy with a platinum group metal and of forming a stable refractory compound phase may be used as a base metal constituent of the alloy. Suitable metals which have been found satisfactory are chromium, beryllium, magnesium, aluminum, silicon, rare earth metals, thorium, uranium and metals in the first, second and third transition series, namely calcium-nickel, strontium-molybdenum and barium-tantalum.

The refractory compound may be an oxide, carbide, nitride, silicide, boride or sulfide or any compound capable of being formed by the interaction of a gaseous phase with the base metal.

The amount of the base metal ingredient or ingredients included in the alloy may vary from a trace to about 5 percent but a total amount from a trace up to no more than 1 percent by weight of the alloy will be found to provide satisfactory results.

The internal treatment in accordance with the invention may be carried out in a number of ways. If the platinum group metal constituent of the alloy or composition consists wholly or predominantly of palladium, the treatment may be carried out with the alloy or composition in the massive form.

If not palladium is present in the alloy or composition, or if palladium does not constitute the predominating metal, it will be found advantageous first to reduce the alloy or composition to powder form by suitable means, such as flame-spraying or electrosparking, before treatment and subsequently to reconstitute it to massive form.

The internal treatment of the alloy or composition may be effected by heating the alloy in the presence of a suitable gas depending on the particular compound to be formed. Thus, if internal oxidation be required, air or oxygen is used and nitrogen or a carburizing gas such as ethane or ethylene is used if a nitride or carbide dispersion be desired.

EXAMPLE I

A palladium alloy containing 0.2 percent by weight of chromium may be fully oxidized in the massive form by heating the alloy in air or oxygen at a temperature of 900° to 1,200° C. in order to cause complete internal oxidation of the chromium constituent.

The following table illustrates the extent and type of oxidation of the above alloy at different temperatures in air, and clearly indicates that complete oxidation is achieved at 1,200° C. as stated above.

TABLE I.

Alloy: Pd/0.2% Cr. (thickness=0.050")

	49½ hrs. at 900° C.	98½ hrs. at 900° C.	50 hrs. at 1,000° C.	98 hrs. at 1,000° C.	117½ hrs. at 1,200° C.	51 hrs. at 1,300° C.	118 hrs. at 1,300° C.	50 hrs. at 1,400° C.	118½ hrs. at 1,400° C.
Heat treatment									
Oxidation type	G.B., T.C.	G.B., T.C.	G.B., T.C.	G.B., T.C.	G.B., T.C.	Mainly T.C.	Mainly T.C.	T.C.	T.C.
Penetration	200	240	340	500		Oxidised throughout specimen			

NOTE: G.B.=Grain boundary oxide; T.C.=Transcrystalline oxide.

EXAMPLE 2

A 15-ounce charge of platinum was melted under pure argon in an induction furnace, and 0.05 percent by weight of zirconium added to the melt, which was cast under the same protective atmosphere into a copper ingot mould.

The ingot thus produced was cold-rolled to sheet 0.040 inch thick, samples of which were annealed in air at various temperatures. A typical example of the effects observed is shown in FIG. 1, where internal oxidation is seen to occur around the grain boundaries and also within the body of the grains.

The rate of oxygen penetration into the zirconium platinum alloy was found to be very low although considerable surface hardening occurred. After 160 hours at 850° C. surface hardness values of 160 H_v were recorded.

EXAMPLE 3

Noble metal alloys containing more than 75 percent by weight of palladium are known to suffer from hydrogen embrittlement and this has been interpreted as an indication that this metal is capable of taking oxygen into solid solution at high temperatures.

In this Example, attempts were therefore made to accelerate the rate of oxygen penetration into platinum by adding to it significant quantities of palladium and also rhodium.

Platinum alloys containing 10 percent of palladium and 0.2 percent of aluminum and also 10 percent of rhodium and 0.2 percent of beryllium were made up by melting under an argon atmosphere and the resultant ingots were rolled to 0.060-inch thick sheet. Samples of the sheet were then annealed in air at temperatures ranging from 900° C. to 1,400° C. At the conclusion of the heat treatments the samples were sectioned and microhardness traverses were made across the traverse surfaces thus exposed.

FIG. 2 illustrates the changes of hardness observed. After 98 hours at 900° C. the alloy containing 10 percent of palladium and 0.1 percent of aluminum developed a surface hardness of 123 H_v, a value considerably higher than that obtained on the annealed unoxidized alloy. This hardening effect penetrated 75 microns below the surface of the sheet test specimens.

Higher temperatures were needed to obtain comparable hardness increases for the rhodium-bearing alloy. Heat treatment in air for 98 hours at 1,400° C. increased the surface hardness from 125 H_v to 155 H_v. Here again oxygen penetration was limited to the outer 75 microns of the specimens.

These results demonstrated that palladium increased the rate of penetration of oxygen into platinum more rapidly than rhodium and that thin platinum alloy sheet could be effectively hardened by internal oxidation. For the purposes of comparison, curves showing the hardening effects caused by the internal oxidation of beryllium-palladium and aluminum-palladium are shown in FIG. 2. Although oxidation has proceeded more rapidly inside these palladium alloys, the surface hardening effects are much less pronounced.

EXAMPLE 4

Platinum was alloyed as in Example 2 with 0.08 percent of titanium and the ingot so produced was worked to rod and sheet. A heat treatment of 50 hours at 1,400° C. in air increased the hardness of the annealed sheet from 50 to 75 H_v. Microexamination showed that the oxidized layer was 40 microns thick. The microstructure of this oxidized layer is illustrated in FIG. 3.

EXAMPLE 5

Bar specimens from the ingot prepared as indicated in Example 4 were swaged to rod approximately 1 cm. in diameter. Two such rods were assembled as electrodes in an electrospark erosion machine and disintegrated under an organic dielectric (white spirit) to fine powder, the bulk of which was less than 2 microns in diameter. Analysis showed that this powder contained 0.07 percent of carbon, indicating that approximately 85 percent of the titanium had under the action of electroerosion reacted with carburizing vapors from the dielectric to form titanium carbide.

After vacuum drying, this powder was pressed together and sintered for 16 hours at 1,400° C. in a vacuum, repressed and resintered to form an ingot having a density of approximately 80 percent of the theoretical value.

The ingot thus obtained was hot-forged in air at 1,400° C. to rod approximately 0.25 inch in diameter. This rod was then cold-swaged and drawn to wire 0.040 inch in diameter.

The creep results obtained on such wire have been compared with those obtained from pure platinum and a rhodium-plating alloy produced by conventional methods in the table below.

TABLE II

Stress (p.s.i.)	Tensile creep tests at 1,400° C. (Life in Hours).		
	Platinum	10% Rhodium-platinum	Carburized Wire
700	1/2-1	40-60	300-500
1400	—	10	150-200
2800	—	1	10

From Table II it will be seen that the creep life for the carburized wire is very considerably improved when compared with the other samples tested.

In the case of platinum-containing alloys, which oxidize more slowly than palladium alloys, it will be found preferable to reduce the cast alloy to powder form before initiating the oxidizing treatment. When oxidation is complete, the powdered alloy is then compacted and sintered at an elevated temperature. The sintered compact is then subjected to severe hot-working, for example, hot-forging or extrusion, to densify the material, and finally cold-worked to the required form.

Platinum group metal alloys embodying, or when made by the method of, the invention will be found to possess considerably improved properties at ambient or high temperatures compared with existing platinum group metal alloys, particularly as regards mechanical strength and to be particularly suitable for use not only in the glass industry, as hereinbefore mentioned, but also for certain structural parts of jet engines, rocket motors, sparking plugs and glow plugs, and for furnace windings, and catalyst gauzes for chemical processes, such as the manufacture of nitric acid and hydrochloric acid. The improved alloys may also be found advantageous for use as electrical contact material.

We claim:

1. A method of making an alloy exhibiting the properties of oxidation resistance and high mechanical strength which comprises alloying a metal selected from the group consisting of platinum, rhodium and their mixtures, alone and alloyed with palladium, with at least one member capable of forming a stable refractory compound and selected from the group consisting of beryllium, magnesium, aluminum, silicon, thorium, uranium, metals in the first transition series consisting of calcium through nickel, metals in the second transition series consisting of strontium through molybdenum and metals in the third transition series consisting of barium through tantalum, said member being present in an amount ranging from a trace to 5 percent by weight of said alloy, heating said alloy in the presence of a gas containing molecular oxygen at a temperature ranging from about 900° to at least 1,200° C. whereby said stable refractory compound is formed internally of said alloy and is dispersed uniformly therethrough.

2. The method of claim 1 wherein said alloy, heated in the presence of a gas containing molecular oxygen, is in powder form.

3. A method of making an alloy exhibiting the properties of oxidation resistance and high mechanical strength which comprises alloying a metal selected from the group consisting of platinum, rhodium, and their mixtures, alloyed with palladium, with at least one member capable of forming a stable refractory compound and selected from the group consisting

of beryllium, magnesium, aluminum, silicon, thorium, uranium, metals in the first transition series consisting of calcium through nickel, metals in the second transition series consisting of strontium through molybdenum and metals in the third transition series consisting of barium through tantalum, said member being present in an amount ranging from a trace to 5 percent by weight of said alloy, heating said alloy in massive form in the presence of a gas containing molecular oxygen at a temperature ranging from about 900° to at least 1,200° C. whereby said stable refractory compound is formed internally of said alloy and is dispersed uniformly therethrough.

4. A method of making an alloy exhibiting the properties of oxidation resistance and high mechanical strength which comprises alloying a metal selected from the group consisting of platinum, rhodium and their mixtures alloyed with palladium, with at least one member capable of forming a stable refractory compound and selected from the group consisting of zirconium, aluminum, beryllium, and titanium, the said member being present in an amount ranging from a trace up to 5 percent by weight of the said alloy, heating said alloy in the presence of a gas containing molecular oxygen at a temperature ranging from about 900° to at least 1,200° C. whereby said stable refractory compound is formed internally of said alloy and is dispersed uniformly therethrough.

5. A method according to claim 4 wherein the alloy comprises 89.8 percent platinum, 10 percent palladium and 0.2 percent aluminum, and where heating is carried out in an argon atmosphere.

6. A method according to claim 4 wherein the alloy comprises 89.8 percent platinum, 15 percent rhodium and 0.2 percent beryllium and wherein heating is carried out in an argon atmosphere.

7. A method according to claim 4 wherein the alloy comprises 89.92 percent platinum, 10 percent palladium and 0.08 percent titanium and wherein the heating is carried out in an argon atmosphere.

8. The method of claim 4 wherein said alloy being heated is in massive form.

9. The method of claim 4 wherein said alloy being heated is in powder form and which method includes; subsequent to heating said powdered alloy whereby said stable refractory compound is formed internally thereof and dispersed uniformly therethrough, forming an ingot by pressing and sintering said powdered alloy and thereafter hot-forging the ingot.

10. A material consisting essentially of an alloy of metal selected from the group consisting of platinum, rhodium and their mixtures with palladium, and a stable refractory compound formed internally of said alloy and dispersed uniformly therethrough, said stable refractory compound being an oxide of a metal selected from the group consisting of zirconium, aluminum, beryllium and titanium, said oxide being present in said alloy in amounts ranging from trace to 5 percent by weight of said alloy, calculated on an elemental metal basis.

* * * * *